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(54) **A process for preparing a metal containing resin composition and the use of the composition thus prepared as a resinous vehicle in antifouling paint.**

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Description

The present invention relates to the preparation of a metal containing resin composition which is characterized by having metal ester bonding at the end portion of a pendant chain. The invention also concerns the use of the thus formed metal containing resin composition as resinous vehicle in antifouling paint.

Today, it is a very common to apply onto ship's bottom an antifouling coating composition comprising an organic or inorganic antifouling agent and a resinous binder as vinyl resin or alkyd resin.

In that case, since the antifouling effect is fully dependent on the antifouling agent dissolved out of the coating and the dissolution of said agent is primarily a diffusion phenomenon caused by a concentration gradient of said agent in the coating, there cannot be expected a long lasting, stable antifouling effect with them.

Furthermore, since the water insoluble resinous component will, after dissolution of said agent from the coating, form a skeleton structure, there are additional problems as increase in resistance of friction between the ship surface and water, lowering of speed and increase in fuel consumption. Under the circumstances, an antifouling coating composition comprising an antifouling agent and a hydrolyzable resin vehicle capable of forming a comparatively tough coating and being gradually decomposed by hydrolysis in sea water has become the center of public attention.

The present inventors had already found that a class of polyester resins having a number of metal-ester bondings in their polyester backbone chains are useful as a resinous vehicle in a polishing type antifouling paint (Japanese Patent Application Nos. 165922/81 and 196900/83).

Such resins are of the nature of being easily hydrolyzed, under weak alkaline condition as in sea water, at the metal-ester bonding portions, disintegrating into a number of small, low molecular weight segments which dissolve in sea water. However, said resins are primarily of comparatively low molecular weight (e.g. up to about 2000) and are poor in film-forming property, and therefore, said coating compositions still have the problems of easy occurrence of cracks and peeling of the formed coatings.

If the molecular weight of said polyester resin is increased to a moderate level, it is indeed possible to improve the film-forming property, but then there will be a marked decrease in hydrolysis property of the resin. To compensate the same, if the metal-ester bonding in the backbone chain of the resin is increased in number, there will give additional problems that the resulting resin is only soluble in a polar solvent and not in most solvents commonly used in a coating composition, and that the formed coating is swollen with sea water. These attempts would therefore, give no fruitful results, and thus, there leaves much to be desired.

An attempt has also been made to use a resin whose side chain has a trialkyl tin ester portion as a terminal group. In this type of resin, polarity of the resin is gradually increased in proportion to the progress in hydrolysis of said ester portion, and the resin is finally dissolved in sea water.

Typical examples of such resins are acrylic resins having as a constitutional element tri organo tin salts of α , β -unsaturated acids. In this case, in order to obtain a stabilized, tough coating, the resin should preferably be free from hydrophilic groups if circumstances allow, and in order to ensure the dissolution of the hydrolyzed resin in sea water, the resin should preferably have as many hydrophilic groups as possible, i.e. more than a certain critical range, after said hydrolysis.

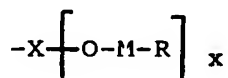
Therefore, in the preparation of such resin by the copolymerization of tri organo tin salt of α , β -unsaturated acid and other acrylic vinyl monomers, attempts have been made such that the former is presented in a higher concentration in the reaction system and the latter is selected from the members with no or only a minor amount of hydrophilic groups. Thus, a copolymer of acrylate, acrylamide, styrene and the like containing 55 to 70 wt% of tri organo tin salt of α , β -unsaturated monobasic acid has been prepared and practically used.

In this type of resin, differing from the aforesaid polyester resin having metal-ester bondings in its main chain, hydrophilic carboxyl groups are generated at the time when the tri organo tin portions at the side chains are released through hydrolysis and the resin is only dissolved in sea water at the stage where the concentration of said carboxyl groups get to a certain critical point. The film-forming property of the resin is also excellent. However, there remains a problem that a considerable quantity of highly expensive and toxic organo tin compound is essential.

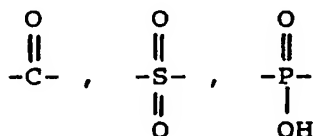
Therefore, from both hygienic and economic point of view, it is desirable to reduce the amount of such material.

Under the circumstances, the inventors have offered previously (Japanese Patent Application No. 106434/85), as a hydrolyzable resin composition which has an excellent film-forming property and which resin is characterized by having at the side chain portions a particular group capable of providing a

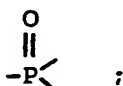
hydrophilic group through hydrolysis, being hydrolyzed and dissolved in sea water at an appropriate rate, and being prepared without the necessity of using a tri organo tin compound, a composition consisting essentially of a resin having at least one side chain bearing at least one terminal group of the formula:



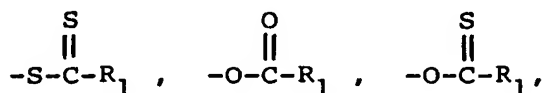
wherein X represents



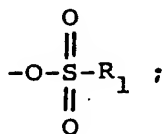
or



M is a metal selected from zinc, copper and tellurium; x is an integer of 1 to 2; R represents an organic acid residue selected from



-O-R₁, -S-R₁ or



and R₁ is a monovalent organic residue.

The said resin composition had been prepared by either one of the following methods.

(1) A mixture of (a) a metal oxide, hydroxide, sulfide or chloride, (b) a monovalent organic acid or its alkali metal salt, and (c) a polymerizable unsaturated organic acid or its alkali metal salt is heated under stirring at a temperature lower than the decomposition temperature of the desired metal ester product, and the by-produced substances as alkali metal chloride, water, monovalent organic acid metal ester and bifunctional polymerizable unsaturated organic acid metal salt are removed to obtain a purified metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid.

Thus obtained metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid or the mixture of said metal ester and the monovalent organic metal ester is then subjected to a homopolymerization or a copolymerization with other copolymerizable monomer(s) to give the desired resin having at least one side chain bearing at least one metal ester containing terminal group.

(2) A mixture of (d) a resin having a side chain an organic acid or its alkali metal salt, (e) a metal oxide, hydroxide, sulfide or chloride, and (f) a monovalent organic acid is heated under stirring at a temperature

lower than the decomposition temperature of the desired metal ester containing resin, and the by-produced substances are removed, if desired, to obtain a resin having at least one side chain bearing the desired metal ester terminal group.

(3) Alternatively, the desired product may be prepared by reacting a resin having at a side chain an organic acid (g) and a monovalent organic acid metal ester (h) at a temperature of not higher than the decomposition temperature of the desired product, thereby effecting an ester exchange reaction between the materials used.

However, various unsolved questions are still remaining in these methods. That is, in the first method, there is a case wherein the selected metal compound happen to exert a polymerization inhibiting activity and a quantity of initiator must be present in the reaction system to accelerate the reaction smoothly.

Furthermore, certain monomers are hardly soluble in a conventional reaction solvent and in such case, the reaction must be carried out under heterogeneous reaction conditions or in a considerable quantity of solvent, giving polymers with low molecular weights.

In the second method, since the reaction involved is a neutralization reaction, there is a considerable difficulty in the control of reaction speed and in the extreme case, there occurs gelation of the reaction product.

And, in this third method, since the reaction involved is a kind of equilibrium reaction and no particular regard is paid to removed by-produced monobasic acid out of the reaction system, such acid always remain in the product in the form of free acid and causes blisters in the coating exposed to ionic atmosphere. Furthermore, such acid may be reacted with an antifouling agent in a coating composition under preparation and storage conditions, causing a remarkable decrease in quality of the coating composition or the coating prepared therefrom. Free acid may also cause corrosion of base plate.

It is, therefore, an object of the invention to provide a novel method for the preparation of a metal containing resin composition which is totally free from the abovesaid problems. An additional object of the invention is to provide a method in which a variety of metals may be freely used and such metal can be incorporated in a resin in various forms bonded with carboxylic acid, sulfonic acid and phosphoric acid.

A further object of the invention is to provide a method by which a high boiling organic acid can be introduced in side chains of a resin in metal ester form and in a higher reaction yield.

Yet another object of the invention is to provide an anti fouling paint which is excellent in film-forming property, and capable of resulting a coating with no blister and being excellent in polishing and antifouling effects.

According to the invention, the aforesaid objects can be attained with a process for preparing a metal containing resin composition comprising reacting a mixture of (A) an acid group containing base resin, (B) a metallic salt of a low boiling organic acid which has a boiling point of 100 to 240 °C, in which the metal is selected from the members having a valence of 2 or more and an ionization tendency less than those of alkali metals, and (C) a high boiling organic monobasic acid having a boiling point which is at least 20 °C higher than the boiling point of said low boiling organic acid, at an elevated temperature while removing the formed low boiling organic acid out of the system, and the use of the resin composition thus prepared as a resinous vehicle in an antifouling paint.

In the present invention, a base resin having acid groups as carboxylic acid, sulfonic acid or phosphoric acid residue is reacted with a metallic salt of low boiling organic acid and a high boiling organic monobasic acid at an elevated temperature and the by-produced (through ester exchange reaction) low boiling organic acid is removed out of the system through, for example, thermal decomposition, vacuum distillation or azeotropic distillation with water or organic solvent.

The reactions involved are all equilibrium reactions and they are, differing from a vigorous neutralization reaction, easily controlled. Furthermore, there is no fear of remaining a quantity of undesired low boiling acid in the reaction product and there is no problem of requiring a larger quantity of initiator.

Therefore, the present method is very useful for the preparation of hydrolysis type, metal containing resin composition for coating use.

Additional benefit resides in the point that high boiling organic acid can be easily and advantageously introduced in a base resin through metal ester bonding, which is hardly possible by the conventional ester exchange reaction between an acid group containing base resin and metallic ester of an organic monobasic acid.

The base resin used in the present invention may be any of the known, coating-use resins having acid groups at the side chains thereof. Examples are vinyl resins, polyester resins, alkyd resins and epoxy resins.

The metallic salts of low boiling organic acids are metallic salts of organic carboxylic acids, organic sulfonic acids or organic phosphoric acids each having a boiling point of 100 ° to 240 °C. Said metallic

component may be any metal having a valence of 2 or more and an ionization tendency less than those of alkali metals.

Examples are the members belonging to Ib (e.g. Cu, Ag), IIa (e.g. Ca, Ba), IIb (e.g. Zn, Cd, Hg), IIIa (e.g. Sc, Y), IIIb (e.g. Al, In), IVa (e.g. Ti, Zr), IVb (e.g. Sn, Pb, Si), Va (e.g. V, Nb), VIa (e.g. Cr, Mo, W), VIb (e.g. Se, Te), VIIa (e.g. Mn) and VIII (e.g. Fe, Co, Ni) groups of Periodic Table.

Though the metallic salts may likewise be organo metal salts as dibutyl tin acetate or dioctyl tin acetate, they must be of polyorganic acid salt type.

In general, a metallic salt is liable to be decomposed by heating. Therefore, the reaction temperature must be settled in a range which is lower than the decomposition temperature of the metallic salt used.

For this reason, the low boiling organic acid should preferably be easily removed out of the system at a temperature which is lower than the decomposition temperature of the metallic salt and preferably 180 °C or more, by either method of thermal decomposition, vacuum distillation, azeotropic distillation with water or azeotropic distillation with an organic solvent. Particularly preferable low boiling organic acids are acetic acid, propionic acid, oxalic acid, lactic acid, pivalic acid, valeric acid, dimethyl acetic acid, enanthic acid, cyclohexane carboxylic acid, propionic acid, glycolic acid, acrylic acid and methacrylic acid. Their corresponding sulfonic acids and phosphoric acids may likewise be used advantageously.

The metallic salts of low boiling organic basic acids may easily be prepared by the equimolar reaction of metal hydroxide or oxide and an organic acid, or the equimolar reaction of metallic sulfonate, nitrate or halide and an alkali metal salt of organic basic acid.

The high boiling organic monobasic acid has a boiling point which is at least 20 °C higher than that of the low boiling organic acid. More preferably, it should have a bioactivity as fungicidal, antifouling and other similar activities. It may be any organic acid including aliphatic, aromatic, alicyclic and heterocyclic organic acids.

Typical examples are benzoic acid, salicylic acid, 3,5-dichlorobenzoic acid, lauric acid, stearic acid, nitro-benzoic acid, linoleic acid, ricinoleic acid, 12-hydroxy stearic acid, fluoroacetic acid, pulvic acid, abietic acid, mercaptobenzothiazole, O-cresotinic acid, naphthol-1-carboxylic acid, p-phenyl benzene sulfonic acid, p-oxybenzoic acid, chloroacetic acid, dichloroacetic acid, naphthenic acid, β -naphthalene sulfonic acid, naphthol-1-sulfonic acid, 5-chloro- α , α -bis (3,5-dichloro-2-hydroxy phenyl) toluene sulfonic acid, p-phenyl benzoic acid, p-toluene sulfonic acid, p-benzene chlorosulfonic acid, dimethyl dithio carbamic acid, diethyl dithio carbamic acid, dibutyl dithio carbamic acid, lithocholic acid, phenoxy acetic acid, 2,4-dichlorophenoxy acetic acid, oleic acid, versatic acid, nicotinic acid and penicillic acid. The reaction may be easily proceeded by merely mixing the materials and heating the mixture. At that time, it is however, necessary to continuously remove the formed low boiling organic basic acid out of the system by, for example, thermal decomposition, vacuum distillation or azeotropic distillation with water or an organic solvent.

The inventors have also found that the reaction time could be markedly shortened when the reaction is carried out in the presence of 0.01 to 5% by weight, preferably 0.03 to 2% by weight of the resinous solid of an organic tin catalyst or an acid catalyst.

The thus obtained resin composition is stable and free from a detectable amount of low boiling organic basic acid which would cause bisters in the formed film or coating. Since an amount of metal ester bondings are included, the thus formed film or coating can be hydrolyzed under ionic atmosphere.

Therefore, the present resin composition may be used in various technical fields including paint, medicine and agricultural chemical industries, as hydrolyzable, film-forming resin. Among them, particular preference is given to resinous vehicle in an antifouling paint.

Thus, in the second aspect of the invention, is provided an anti fouling paint containing as resinous vehicle a metal containing resin composition prepared by the method of this invention.

In this particular application, since a hydrolysis rate of the resulted coating is very important, the acid group containing base resin should preferably have an acid value of 25 to 350 mg KOH/g. This is because, if the acid value is less than 25 mg KOH/g, the desired hydrolysis rate of the coating may not be fully attained due to deficient metal ester bondings, whereas if the acid value exceeds over 350 mg KOH/g, there are adverse effects on film properties.

As to the molecular weight of the present metal containing resin, there is no particular limit on it. However, when used as a resinous vehicle of an antifouling paint, number average molecular weight of the resin should preferably be settled in a range of 4000 to 40000, and more preferably 6000 to 35000. This is because, if the molecular weight of the resin is less than 4000, there is a fear of the occurrence of cracks and peeling of the formed coating due to the deficient film-forming properties, and if the molecular weight of the resin exceeds over 40000, there is a tendency that storage stability of the coating composition is lowered to an undesirable extent. Moreover, a larger amount of diluting solvent is required for coating purpose and this is not also uneconomical, but also undesired from air-pollution and public health points of

view.

The present antifouling paint is characterized by containing as resinous vehicle the abovementioned metal containing resin composition; however, this paint may further contain, as optional ingredients, the following.

(1) Antifouling agent:

Various known antifouling agents including antifouling agents for ship bottom paint, bactericides, fungicides, agricultural chemicals or the like may be satisfactorily used. However, when the solubility of such compound in sea water is less than 0.01 ppm, it is unable to get a good balance between the dissolution speed of the coating and dissolving power of the antifouling agent, and therefore, no effective antifouling can be expected with said compound. On the other hand, when the solubility of such compound in sea water is over 5000 ppm, the formed coating will absorb water and the contained antifouling agent will selectively dissolve out and hence, it is unable to get a desired antifouling efficiency.

Therefore, the solubility of antifouling agent in sea water should preferably be in a range of 0.01 to 5000 ppm, and more preferably 0.1 to 50 ppm.

Examples of such antifouling agents are powder or flake form of copper, zinc or manganese; oxides, suboxides, rhodanides, carbamates, hydroxides or pyrrhionones of copper, zinc or manganese; benzothiazole compounds; phthalimide compounds; sulfamide compounds; sulfide compounds; quinoline compounds; phthalonitrile compounds; carbamate compounds; isothiazoline compounds; triphenyl tin compounds; carbamic acid compounds and esters; and thiocyanate compounds.

(2) Plasticizer and hydrolysis regulator:

As the plasticizer and hydrolysis regulator, any of the known members having solubility in sea water of 0 to 1 % by weight may be satisfactorily used.

This is because, if the solubility is over 1% by weight, the used plasticizer and hydrolysis regulator are selectively dissolved out of the coating to sea water and stable plasticising and polishing effects can hardly be obtained.

Examples of such plasticizers are phthalic acid esters as dioctyl phthalate, dimethyl phthalate and dicyclohexyl phthalate; aliphatic dibasic acid esters as diisobutyl adipate and dibutyl sebacate; glycol esters as diethylene glycol dibenzoate and pentaerythritol alkyl ester; phosphoric acid esters as tricresyl phosphate and trichloroethyl phosphate; epoxy type plasticizers as epoxy soyabean oil and epoxy octyl stearate; organo tin plasticizers as dioctyl tin laurate and dibutyl tin laurate; trioctyl trimellitate, camphor and triacetylene.

(3) Hydrolysis regulator:

Examples of such hydrolysis regulators are chlorinated paraffin, polyvinyl ether, polypropylene sebacate, partially hydrogenated terphenyl, polyvinyl acetate, polyalkyl (meth) acrylate, polyether polyol, alkyd resin, polyester resin and polyvinyl chloride.

(4) Pigment:

For example, body pigments as baryte, precipitated barium sulphate, talc, kaoline, chalk, silica white, alumina white, titanium white and bentonite; color pigments as titanium dioxide, zirconium oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide, chrome green, emerald green and phthalocyanine blue.

(5) Solvent:

For example, hydrocarbons (e.g. xylene, toluene, benzene, ethyl benzene, cyclopentane, octane, heptane, cyclohexane and white spirit), ethers (e.g. dioxan, tetrahydrofuran, ethyleneglycol monomethyl ether, ethyleneglycol monoethyl ether, ethyleneglycol dimethyl ether, ethyleneglycol monobutyl ether, ethyleneglycol dibutyl ether, diethyleneglycol monomethyl ether and diethyleneglycol monoethyl ether), esters (e.g. butyl acetate, propyl acetate, benzyl acetate, ethyleneglycol monomethyl ether acetate and ethyleneglycol monoethyl ether acetate), ketones (e.g. methyl isobutyl ketone and ethyl isobutyl ketone), and alcohols (e.g. n-butanol and propyl alcohol).

(6) Other additives:

For example, organic monobasic acids (e.g. rosin, monobutyl phthalate and mono-octyl succinate), camphor and castor oil.

5 The antifouling paint can be prepared by the method known per se in the art, by using ball-mil, pebble mil, roll mil or speed run mil.

The present inventors have also found that by the inclusion of 0.01 to 5 wt% of amphoteric group containing compound as described in Japanese Patent Application Laid Open No. 151727/56 in the present coating composition (as exemplified in Examples 19 to 58), it is possible to shorten the dispersing time
10 required for the formulation of said paint and improve the dispersion stability of thus obtained paint.

Since the vehicle resin contains metals, whose ionization tendency is lower than those of alkali metals, as zinc, copper or tellurium in the form of metal esters, the coating or film obtained will be gradually hydrolyzed in an alkali atmosphere as in sea water, and disintegrated and dissolved or dissipated in said atmosphere.

15 Furthermore, differing from the known hydrolysis type polyester resin having metal ester bonds in main chain, the present resin is characterized by having the metal ester bonds at the end portions of side chains.

Therefore, with the progress of hydrolysis of said side chains, the resin is gradually turned to soluble type resin and finally dissolved in sea water. Thus, the solubilization mechanism involved totally differs from that of known hydrolysis type polyester resin which is disintegrated to small pieces by hydrolysis. For this
20 reason, the present anti fouling paint could exhibit a longer effective life than the conventional one. Furthermore, since the present anti fouling paint can be formulated without the necessity of being fully relied on an expensive and toxic triorgano tin compound, the manufacturing cost can be markedly lowered and hygienic problems can be effectively obviated.

The present paint is totally free from low boiling organic basic acid and therefore, there is no fear of
25 forming blisters in the formed coating. Thus, the present antifouling paint is quite useful for the coating of various substrates as ships, marine structures and fish nets.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and % are by weight.

30 Preparation of base resin varnishes

Reference Example 1

Into a 4-necked flask fitted with a stirrer, a reflux condenser, a nitrogen gas inlet tube and a dropping
35 funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 110° to 110°C. To this, a mixture of 25.7 parts of acrylic acid, 57.8 parts of ethyl acrylate, 16.5 parts of methyl methacrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the combined mixture was maintained at 110°C for 30 minutes, added dropwise with a mixture of
40 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then maintained at the same temperature for 2 hours to obtain a resinous varnish (A) having a solid content of 39.6 wt % and a solid acid value of 200 mg KOH/g. The number average molecular weight (polystyrene conversion) of the resin contained was 11000.

Reference Example 2

45 Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 90 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110°C. To this, a mixture of 7.7 parts of methacrylic acid, 64.4 parts of methyl methacrylate, 28 parts of 2-ethyl hexyl acrylate and 2 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of
50 said addition, the mixture was heated at 110°C for 30 minutes, added dropwise with a mixture of 30 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (B) having a solid content of 39.8 wt % and a solid acid value of 50 mg KOH/g. The number average molecular weight of the resin contained was 15000.

55 Reference Example 3

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to

110 °C. To this, a mixture of 38.5 parts of acrylic acid, 50.9 parts of ethyl acrylate, 10.6 parts of n-butyl acrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 110 °C for 30 minutes, dropwise added with a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (C) having a solid content of 39.4 wt % and a solid acid value of 300 mg KOH/g. The number average molecular weight of the resin contained was 12000.

Reference Example 4

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 80 parts of xylene and 20 parts of n-butanol and the mixture was heated to 80 ° to 90 °C. To this, a mixture of 38.5 parts of acrylic acid, 45.8 parts of ethyl acrylate, 15.7 parts of methyl methacrylate and 1.5 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 90 °C for 30 minutes, dropwise added with a mixture of 40 parts of xylene, 10 parts of n-butanol and 0.5 parts of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (D) having a solid content of 39.8 wt% and a solid acid value of 300 mg KOH/g. The number of average molecular weight of the resin contained was 37000.

Example 1

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 25.9 parts of zinc acetate, 40.3 parts of oleic acid and 120 parts of xylene and the mixture was heated to 120 °C and maintained at the same temperature, while removing the formed acetic acid with said solvent. The end point of said reaction was settled by determining the quantities of acetic acid in the distillate and the reaction was stopped after elapsing 12 hours. Thus obtained varnish-1 had a solid content of 55.3 wt% and a viscosity of R-S.

Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 44 parts of copper propionate, 60 parts of naphthenic acid, 0.1 part of butane sulfonic acid and 20 parts of deionized water and the mixture was heated to 100 °C and maintained at the same temperature, while removing the formed propionic acid azeotropically with water. The end point of said reaction was determined by checking the amount of propionic acid in the distillate. The remaining amounts of water were completely removed, the reaction was stopped after 7 hours' reaction and xylene was then added to the reaction mixture. Thus obtained varnish-2 had a solid content of 52.3 wt% and a viscosity of P.

Example 3

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a decanter, were placed the resinous varnish (B) obtained in Reference Example 2, 8.1 parts of manganese acetate and 7.8 parts of 2,4-dichlorophenoxy acetate and the mixture was heated to 70 °C and maintained at the same temperature for 10 hours. The formed acetic acid was continuously removed under reduced pressure and, after completion of the reaction, 95 parts of xylene were added to obtain varnish-3 having a solid content of 56.3 wt% and a viscosity of U.

Example 4

Into a similar reaction vessel as used in Example 1, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 37.2 parts of cobalt acetate, 32.1 parts of versatic acid and 120 parts of xylene and the mixture was heated and reacted while removing the formed acetic acid with the solvent for 12 hours. Thus obtained varnish-4 had a solid content of 56.2 wt% and a viscosity of Y.

Example 5

The similar experiment as stated in Example 4 was repeated excepting substituting 65.1 parts of germanium acetate for 37.2 parts of cobalt acetate and 186 parts of versatic acid for 32.1 parts of versatic acid. Thus obtained varnish-5 had a solid content of 54.8 wt% and a viscosity of Z.

Example 6

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 22 parts of vanadium oxalate, 41.5 parts of naphthenic acid and 130 parts of xylene, and the mixture was heated to 120 °C and reacted at the same temperature while removing the formed oxalic acid with the solvent. Thus obtained varnish-6 had a solid content of 52.8 wt% and a viscosity of P.

Example 7

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 42.5 parts of zinc dl-lactate trihydrate, 28.6 parts of SA-13 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon number 13) and 100 parts of xylene and the mixture was heated to 120 °C and reacted at the same temperature while removing the formed lactic acid with xylene. Thus obtained varnish-7 had a solid content of 54.2 wt% and a viscosity of Q.

Example 8

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 37 parts of nickel valerate, 22.6 parts of SA-9 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon atoms 9), and 95 parts of xylene and the mixture was heated to 140 °C and reacted at the same temperature while removing the formed valeric acid with xylene. Thus obtained varnish-8 had a solid content of 55.1 wt% and a viscosity of O.

Example 9

The same procedures as stated in Example 3 were repeated excepting substituting a mixture of 100 parts of the resinous varnish (C) obtained in Reference Example 3, 99.1 parts of lead enanthate and 62 parts of versatic acid for the materials shown in Example 3 and changing the reaction temperature to 140 °C. Thus obtained varnish-9 had a solid content of 52.7 wt% and a viscosity of R.

Example 10

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (B) obtained in Reference Example 2, 9.9 parts of magnesium cyclohexane carboxylate, 4.4 parts of nicotinic acid and 20 parts of deionized water and the mixture was reacted as in Example 2. Thus obtained varnish-10 had a solid content of 53.4 wt% and a viscosity of R.

Example 11

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 39.9 parts of aluminium cyclopropane carboxylate, 72.4 parts of 2,4-dichlorophenoxy acetate and 125 parts of xylene and the mixture was heated to 140 °C and reacted as in Example 1, to obtain varnish-11 having a solid content of 51.8 wt% and a viscosity of V.

Example 12

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 34.7 parts of tellurium

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acetate, 40 parts of naphthenic acid, 0.2 part of butylene sulfonic acid and 110 parts of xylene and the mixture was reacted as in example 1 for 8 hours to obtain varnish-12 having a solid content of 52.4 wt% and a viscosity of S.

5 Example 13

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (B) obtained in Reference Example 2, 10.4 parts of dibutyl tin acetate, 7.1 parts of SA-13 and 115 parts of xylene and the mixture was reacted as in Example 1 to obtain
10 varnish-13 having a solid content of 53.4 wt% and a viscosity of N.

Example 14

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter,
15 were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 32.4 parts of chromium acetate, 80.7 parts of oleic acid and 130 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-14 having a solid content of 51.8 wt% and a viscosity of U.

Example 15

20 Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 62.1 parts of dibutyl tin acetate, 62.1 parts of versatic acid and 150 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-15 having a solid content of 54.7 wt% and a viscosity of X.

25 Example 16

Using a resinous varnish (B) obtained in Reference Example 2, 10 parts of titanium acetate, 18.2 parts of penicillic acid and 50 parts of xylene and the reaction temperature of 75° to 90°C, the similar
30 experiment as stated in Example 3 was repeated to obtain varnish-16 having a solid content of 52.8 wt% and a viscosity of Y.

Example 17

35 Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 59.9 parts of titanium acetate, 101 parts of 2,4-dichlorophenoxy acetate and 180 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-17 having a solid content of 56.2 wt% and a viscosity of Z.

40 Example 18

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 40 parts of copper acetate, 60 parts of naphthenic acid and 110 parts of xylene and the mixture was heated at 120°C while
45 removing the formed acetic acid with the solvent. Thus obtained varnish-18 had a solid content of 39.6 wt% and a viscosity of W.

Comparative Example 1

50 The resinous varnish (C) obtained in Reference Example 3 was used as it is as Comparative varnish-1.

Comparative Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping
55 funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110°C. To this, a mixture of 30 parts of ethyl acrylate, 70 parts of methyl methacrylate and 2 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition and heating at 110°C for 30 minutes, a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of

azobisisobutyronitrile was dropwise added in 1 hour and the combined mixture was heated at the same temperature for 2 hours to obtain Comparative varnish-2 having a solid content of 39.6 wt%.

Comparative Example 3

5

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 10.3 parts of zinc hydroxide, 60 parts of oleic acid and 110 parts of xylene and the mixture was heated at 100 to 120 °C while removing water with the solvent. Thus obtained varnish (Comparative varnish-3) had a solid content of 55.8% and a viscosity of Z₂.

10

Comparative Example 4

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a nitrogen gas inlet tube, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1 and 68 parts of zinc oleate, and the mixture was reacted at 120 °C for 3 hours. Thus obtained varnish (Comparative varnish-4) had a solid content of 62% and a viscosity of M to N.

15

Comparative Example 5

20

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 13 parts of zinc hydroxide and 105 parts of xylene and the mixture was heated at 120 °C. During the reaction, certain amounts of water were distilled off, but after elapsing 30 minutes from the commencement of said reaction, the content was turned to gel and no uniform resinous solution was obtained.

25

Comparative Example 6

Into a similar reaction vessel as used in Comparative Example 1, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 16.6 parts of copper hydroxide, 60 parts of naphthenic acid and 110 parts of xylene and the mixture was heated at 120 °C while removing water with the solvent. After elapsing 2 hours from the commencement of the reaction, the content was turned to gel and no uniform resinous solution was obtained.

30

Example 19

35

45 parts of varnish-1 obtained in Example 1, 30 parts of cuprous oxide, 5 parts of zinc bis (dimethyl dithiocarbamate), 3 parts of colloidal silica, 5 parts of xylene, 10 parts of methyl isobutyl ketone and 2 parts of n-butanol were placed in a ball mill and the mixture was subjected to a dispersion operation for 5 hours to obtain a coating composition containing particles with maximum diameter of 35 μm.

40

Example 20 to 58 and Comparative Examples 5 to 9 Using the materials shown in Table 1 and following the method stated in Example 19, the respective coating composition was prepared.

45

50

55

Table 1

	Example	20	21	22	23	24	25	26
5	varnish 1	35	30					
	varnish 2			40	45			
	varnish 3					25		
	varnish 4						40	
	varnish 5							35
10	varnish 6							
	varnish 7							
	varnish 8							
	varnish 9							
	varnish 10							
15	Note 1	20			15		15	
	Note 2		20			15		
	Note 3			25				
	Note 4							
	Note 5						3	
20	Note 6		10					15
	Note 7				5			
	Note 8	10						
	Note 9					10		
	Note 10						5	
25	Note 11						10	
	Note 12					5		5
	Note 13							
	Note 14			5				
	Note 15							10
30	Note 16		5			10		
	Note 17							
	Note 18			5				5
	Note 19		5		5			
	Note 20				5	5		
35	Note 21			5				
	Note 22					5		
	Note 23	5	5	5	2			
	Note 24	10		5	5		5	10
	Note 25	5	5	5	3		5	
40	Note 26	3	3	3	3	3	3	3
	Note 27		10					
	Note 28	10	5		5	20	10	10
	Note 29	2	2	2	2	2	4	2
	total	100	100	100	100	100	100	100

Table 1 (continued)

	Example	27	28	29	30	31	32
5	varnish 1						
	varnish 2						
	varnish 3						
	varnish 4						
	varnish 5						
10	varnish 6	30					
	varnish 7		35				
	varnish 8			30			
	varnish 9				35		
	varnish 10					40	45
15	Note 1	25		30		20	
	Note 2				30		
	Note 3		20				
	Note 4	5					
	Note 5				5		
20	Note 6						10
	Note 7			10		5	
	Note 8					5	
	Note 9						
	Note 10						
25	Note 11						
	Note 12				10		15
	Note 13		10				
	Note 14	5					
	Note 15						
30	Note 16				5		
	Note 17		10	5			
	Note 18	5					10
	Note 19	5	5				
	Note 20	5		5			
35	Note 21		5				
	Note 22				5		
	Note 23	5	5				
	Note 24			5		5	
	Note 25	5					
40	Note 26	3	3	3	3	3	3
	Note 27	5		5	5	10	5
	Note 28		5	5		10	10
	Note 29	2	2	2	2	2	2
45	total	100	100	100	100	100	100

50

55

Table 1 (continued)

	Example	33	34	35	36	37	38	39	40	41	42
5	varnish 1	35	40								
	varnish 2			35	40						
	varnish 3					35	40				
	varnish 9							40			
	varnish 10								35		
10	varnish 11									40	
	varnish 12										35
	varnish 13										
	varnish 14										
	varnish 15										
15	varnish 16										
	varnish 17										
	varnish 18			10							
	Note 1'	25				10	15		5		
	Note 2'				25						15
20	Note 3'		30			15		10	10		
	Note 4'			25				15		15	
	Note 5'			10							
	Note 6'		15					5			
	Note 7'								10		
25	Note 8'					10				10	
	Note 9'	10			10		5				
	Note 10'										5
	Note 11'										
	Note 12'						5				
30	Note 13'										
	Note 14'										5
	Note 15'										
	Note 16'					5					
	Note 17'			5							
35	Note 18'							10			
	Note 19'		5							5	
	Note 20'			5	5	10	10			10	10
	Note 21'	5					5		10		5
	Note 22'			5	5	5			10	5	5
40	Note 23'	10	5		10		5	5	5	5	10
	Note 24'	3	3	3	3	3	3	3	3	3	3
	Note 25'	10				5	10	10	10	5	5
	Note 26'	2	2	2	2	2	2	2	2	2	2
	total	100	100	100	100	100	100	100	100	100	100

Table 1 (continued)

	Example	43	44	45	46	47	48	49	50	51
5	varnish 1									
	varnish 2								10	5
	varnish 3									
	varnish 9									
	varnish 10									
10	varnish 11									
	varnish 12									
	varnish 13	35								
	varnish 14		40							
	varnish 15			40						
15	varnish 16				45					
	varnish 17					40				
	varnish 18						45	40	30	35
	Note 1'	15		15				25	20	
	Note 2'		5			15	20			25
20	Note 3'		10						5	
	Note 4'									
	Note 5'									
	Note 6'									
	Note 7'				15					
25	Note 8'					10				
	Note 9'							5		
	Note 10'									
	Note 11'	10					10	10		
	Note 12'			10						5
30	Note 13'								10	
	Note 14'									10
	Note 15'	5		5						
	Note 16'					10				
	Note 17'		10		15					
35	Note 18'									
	Note 19'		5							
	Note 20'	10	10	10	15	10	10	10		10
	Note 21'		5						15	
	Note 22'	5		5		5	5		5	
40	Note 23'			5		5	5			5
	Note 24'	3	3	3		3	3	3	3	3
	Note 25'	15	10	5	10			5		
	Note 26'	2	2	2		2	2	2	2	2
45	total	100	100	100	100	100	100	100	100	100

50

55

Table 1 (continued)

	Example	52	53	54	55	56	57	58
5	varnish 1	35	35					
	varnish 2			45	40			
	varnish 3					35	35	
	varnish 4							40
	varnish 15							
10	varnish 16							
	varnish 17							
	varnish 18							
	Note 1"	5					10	
	Note 2"		10					
	Note 3"			5	10			
15	Note 4"		5					10
	Note 5"	10		10			5	
	Note 6"		5					
	Note 7"		10	15			15	
	Note 8"	15				15		25
20	Note 9"		5					
	Note 10"	5						
	Note 11"				5			
	Note 12"						10	
	Note 13"				5			
25	Note 14"					10		
	Note 15"			5				
	Note 16"	5						
	Note 17"		5					
	Note 18"					10		10
30	Note 19"					5		
	Note 20"	5						
	Note 21"	5	10	5	5		5	10
	Note 22"	5	5	5	10	5	5	
	Note 23"	3	3	3	3	3	3	3
35	Note 24"		10	5	10	15	10	
	Note 25"	5			10			
	Note 26"	2	2	2	2	2	2	2
	total	100	100	100	100	100	100	100

Table 1 (continued)

5	<u>Comparative Example</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
	<u>Comparative varnish 1</u>	<u>45</u>				
	<u>Comparative varnish 2</u>		<u>45</u>			
10	<u>Comparative varnish 3</u>			<u>23</u>		
	<u>Comparative varnish 4</u>				<u>45</u>	
15	<u>varnish 1</u>					<u>35</u>
	<u>cuprous oxide</u>	<u>30</u>	<u>30</u>	<u>15</u>	<u>30</u>	
20	<u>Zn bis (dimethyl</u>					
	<u>dithiocarbamate)</u>	<u>5</u>	<u>5</u>	<u>2</u>	<u>5</u>	
	<u>copper sulfate</u>					<u>25</u>
25	<u>dioctyl phthalate</u>					<u>5</u>
	<u>titanium oxide</u>					<u>5</u>
	<u>talc</u>					<u>5</u>
30	<u>xylene</u>	<u>5</u>	<u>5</u>	<u>46</u>	<u>5</u>	<u>10</u>
	<u>colloidal silica</u>	<u>3</u>	<u>3</u>	<u>2</u>	<u>3</u>	<u>3</u>
35	<u>red iron oxide</u>					<u>5</u>
	<u>methyl isobutyl ketone</u>	<u>10</u>	<u>10</u>	<u>10</u>	<u>10</u>	<u>5</u>
40	<u>n-butanol</u>	<u>2</u>	<u>2</u>	<u>2</u>	<u>2</u>	<u>2</u>
	<u>total</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>

45 In Comparative Example 7, paint viscosity was very high, and
 therefore, a larger quantity of xylene was used.

50

55

Note 1 : cuprous oxide

Note 2 : zinc white

5 Note 3: copper rhodanide

Note 4: Cu powder

10 Note 5: Zn powder

Note 6: copper hydroxide

Note 7: 2-thiocyanomethylthio benzothiazole

15 Note 8: N-(fluorodichloromethylthio) phthalimide

Note 9: N-(trichloromethylthio) phthalimide

20 Note 10: N-(tetrachloroethylthio) tetraphthalimide

Note 11: benzyl isothiocyanate

Note 12: quinoline

25 Note 13: 8-hydroquinoline

Note 14: zinc pyrithione

Note 15: triphenyl tin acetate

30 Note 16: bis-triphenyl tin oxide

Note 17: 3-Jod-2-propynyl butyl carbamate

Note 18: tricresyl phosphate

35 Note 19: polyvinyl ether

Note 20: chlorinated paraffin wax

40 Note 21: polyether polyol

Note 22: dioctyl phthalate

Note 23: talc

45 Note 24: titanium oxide

Note 25: red iron oxide

50 Note 26: colloidal silica

Note 27: methyl isobutyl ketone

55

- Note 28: xylene
- Note 29: n-butanol
- 5 Note 1': cuprous oxide
- Note 2': copper rhodanide
- 10 Note 3': zinc white
- Note 4': copper hydroxide
- Note 5': N,N-dimethyl-N'-(fluorodichloromethylthio)
- 15 sulfamide
- Note 6': 2-benzimidazole carbamic methyl
- Note 7': benzyl isothiocyanate
- 20 Note 8': N-n-octyl-isothiazolone
- Note 9': N,N-dimethyl-N'-phenyl-N'-(fluorodicyclomethylthio)
- 25 sulfamide
- Note 10': Zn bis (dimethyl dithiocarbamate)
- Note 11': Zn ethylene bis (dithiocarbamate)
- 30 Note 12': Mn ethylene bis (dithiocarbamate)
- Note 13': Cu bis (dimethyl dithiocarbamate)
- Note 14': 2,4,5,6-tetrachloro-1,3-isophthalonitrile
- 35 Note 15': 2,3,5,6-tetrachloro-4-(methyl sulfonyl) pyridine
- Note 16': 4,5-dichloro-2-n-octyl-4-isothiazoline-3-on
- 40 Note 17': dimethyl dithiocarbamic acid bromide
- Note 18': triphenyl tin hydroxide
- Note 19': triphenyl tin chloride
- 45 Note 20': chlorinated paraffin wax
- Note 21': dioctyl phthalate
- Note 22': titanium oxide
- 50 Note 23': red iron oxide

Note 24': colloidal silica

Note 25': xylene

5 Note 26': n-butanol

Note 1": chlorinated polyethylene

10 Note 2": chlorinated polypropylene

Note 3": triamyl citrate

Note 4": isobutyl tartarate

15 Note 5": polyether polyol

Note 6": copper naphthenate

Note 7": cuprous oxide

20 Note 8": zinc white

Note 9": 2,4-(thiazolyl) benzoimidazole

25 Note 10": 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole

Note 11": phenothiazole

Note 12": α -nitrostyrene sulfathiazole

30 Note 13": nitro acridine

Note 14": sulfathiazole

Note 15": tetraphenyl boron pyridinium

35 Note 16": thiabendazole

Note 17": N-(1,1,2,2-tetrachloroethylthio)-cyclohexene-1,2-
40 d:carboxyimide

Note 18": α -chloro- α -phenyl acetyl urea

Note 19": 2-methyl carboxy-amino-benzimidazole

45 Note 20": talc

Note 21": titanium oxide

50 Note 22": red iron oxide

Note 23": colloidal silica

55

Note 24": xylene

Note 25": methyl isobutyl ketone

Note 26": n-butanol

The coating compositions obtained in Examples 19 to 58 and Comparative Examples 5 to 9 each was applied onto a test plate in about 200 μ dry thickness, and thus prepared test plate was attached to Discrotor, immersed in sea water (16° to 23°C) and rotated at a constant speed (peripheral speed about 30 knots) for 3 months (days and nights). Use-up rate of the coating was determined microscopically. The results are show in Table 2.

Table 2

Example	Coating use-up rate		
	Initial film thickness (μ)	film thickness after 3 months (μ)	used up film thickness (μ)
5	19	190	160
	20	210	185
	21	190	155
	22	190	135
10	23	200	160
	24	200	185
	25	185	160
	26	210	180
	27	170	150
15	28	190	160
	29	180	150
	30	190	155
	31	180	170
20	32	190	175
	33	190	160
	34	185	150
	35	200	160
	36	200	165
25	37	210	190
	38	185	170
	39	190	150
	40	205	195
	41	195	180
	42	185	165
30	43	205	190
	44	210	185
	45	190	160
	46	210	195
	47	195	170
35	48	210	180
	49	205	180
	50	200	170
	51	195	160
40	52	195	160
	53	200	170
	54	190	155
	55	170	130
	56	205	190
	57	205	185
45	58	190	65
	Comp. Ex.		
	7	200	0
	8	190	190
	9	170	135
50	10	190	135
	11	165	95

Next, the respective coating composition was applied twice by brushing onto a sand-blasted steel plate previously coated with an anti-corrosive paint, so as to give a coating of 100 μ dry thickness each time. Thus prepared test plate was immersed in sea water for a defined period of time and the antifouling effect was examined. These tests were conducted at Aioi Bay, Hyogo Pref.. The results are shown in Table 3.

Table 3

Antifouling test

(surface area % adhered with submarine living)

Example	19	20	21	22	23	24	25	26	27	28	29	30	31
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	5	0	0	0	5	0	0	0	0	0	5	0
28	0	15	0	0	5	10	0	5	0	0	0	15	0
30	3	20	0	5	10	15	10	15	0	0	0	20	0

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Example	32	33	34	35	36	37	38	39	40	41	42	43	44
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	5	0	0	0	0	0	0	0	0	0	0	0	0
28	15	0	5	0	0	0	0	3	0	0	0	0	0
30	20	0	15	10	0	3	0	10	10	5	0	0	3

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Example	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Duration (months)														
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	*	*	*	*	*	*	*
28	0	0	0	0	0	0	0	*	*	*	*	*	*	*
30	0	10	3	5	0	0	0	*	*	*	*	*	*	*

* ... unexamined

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Comparative Example	7	8	9	10	11
Duration (months)					
2	0	0	0	0	0
4	0	30	0	0	0
6	100	80	0	0	0
6	100	100	0	0	0
10	100	100	0	0	0
12	stopped	100	10	5	0
14		stopped	30	20	0
16			100	70	30
19			100	100	100
20			100	100	100

Visual examination of surface conditions:

After conducting the aforesaid immersion test, the coated plate was examined by naked eyes on the surface conditions. No blisters and cracks were found on the coated plates of Examples 19 to 58. In Comparative Example 7, cracks were observed after 12 months' immersion test and in Comparative Example 8, blisters were observed after 10 months' immersion test.

The present invention thus provides a novel process for the preparation of metal containing, hydrolysis type resin composition which is very useful as resinous vehicle for an antifouling paint having excellent binder function and well-balanced dissolution properties. This process is quite suitable for the production of such resin compositions with a variety of metal sources in comparatively higher yields. The present resin composition can be freely compounded with a variety of antifouling agents and thus obtained antifouling paints are characterized in resulting coatings which are free from blisters and iron corrosion and give excellent, long-lasting antifouling effects.

Claims

1. A process for preparing a metal containing resin composition, characterized in that a mixture of
 - (A) an acid group containing base resin,
 - (B) a metallic salt of a low boiling organic acid which has a boiling point of 100 to 240 °C, in which the metal is selected from the members having a valence of 2 or more and an ionization tendency less than those of alkali metals, and
 - (C) a high boiling organic monobasic acid having a boiling point which is at least 20 °C higher than the boiling point of said low boiling organic acid

is reacted at an elevated temperature while removing the formed low boiling organic acid out of the system.

2. A process according to claim 1, characterized in that the metal is selected from the members belonging to the groups Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, VIa, VIb, VIIa and VIII of the Periodic Table.
3. A process according to claim 2, characterized in that the metal is selected from zinc, copper and tellurium.
4. A process according to any of claims 1-3, characterized in that the high boiling organic monobasic acid has an antifouling property.
5. A process according to any of claims 1-4, characterized in that the reaction is carried out in the presence of water, while removing the formed low boiling organic acid azeotropically with said water.
6. A process according to any of the claims 1-4, characterized in that the low boiling organic acid is removed under reduced pressure.
7. A process according to any of claims 1-4, characterized in that the reaction is carried out in the presence of an organic solvent and the formed low boiling organic acid is removed out of the system azeotropically with said organic solvent.
8. A process according to any of claims 1-7, characterized in that the acid group containing base resin has an acid value of 25 to 350 mg KOH/g.
9. The use of a metal containing resin composition prepared by the method of any of claims 1-8 as a resinous vehicle in an antifouling paint, said paint containing possible further components which can be selected from organic and/or inorganic antifouling agents, plasticizers, hydrolysis regulators, pigments, solvents and other conventional additives.

Patentansprüche

1. Methode zur Herstellung von einer Metall enthaltenden Harzzusammensetzung, dadurch gekennzeichnet, daß man ein Gemisch
 - (A) eines Säuregruppe enthaltenden Basisharzes,
 - (B) eines Metallsalzes einer niedrigsiedenden organischen Säure mit einem Siedepunkt von 100 bis 240 °C, wobei das Metall aus den Mitgliedern mit einer Valenz von 2 oder mehr und einer Ionisierungstendenz niedriger als die der Alkalimetalle ausgewählt wird, und
 - (C) einer hochsiedenden organischen monobasischen Säure mit einem Siedepunkt, der zumindest 20 °C höher ist als der Siedepunkt der genannten niedrigsiedenden organischen Säure, reagieren läßt bei einer erhöhten Temperatur während die gebildete niedrigsiedende organische Säure aus dem System entfernt wird.
2. Methode nach Anspruch 1, dadurch gekennzeichnet, daß das Metall aus den zu den Gruppen Ib, IIa, IIb, IIIa, IIIb, IVa, Va, VIa, VIb, VIIa und VIII des Periodensystems gehörenden Mitgliedern ausgewählt wird.
3. Methode nach Anspruch 2, dadurch gekennzeichnet, daß das Metall aus Zink, Kupfer und Tellur ausgewählt wird.
4. Methode nach einem der Ansprüche 1-3, dadurch gekennzeichnet, daß die hochsiedende organische monobasische Säure eine bewuchsverhindernde Eigenschaft hat.
5. Methode nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß die Reaktion in Gegenwart von Wasser durchgeführt wird während die gebildete niedrigsiedende organische Säure azeotropisch mit dem genannten Wasser entfernt wird.

6. Methode nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß die niedrigsiedende organische Säure unter erniedrigtem Druck entfernt wird.
7. Methode nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß die Reaktion in Gegenwart von einem organischen Lösungsmittel durchgeführt wird und die gebildete niedrigsiedende organische Säure mit dem genannten organischen Lösungsmittel azeotropisch aus dem System entfernt wird.
8. Methode nach einem der Ansprüche 1-7, dadurch gekennzeichnet, daß das Säuregruppe enthaltende Basisharz einen Säuregrad von 25 bis 350 mg KOH/g hat.
9. Anwendung einer Metall enthaltende Harzzusammensetzung, hergestellt gemäß der Methode gemäß einem der Ansprüche 1-8, als ein Pigmentträger in einer bewuchsverhindernden Anstrichfarbe, wobei die genannte Anstrichfarbe mögliche weitere Komponenten umfaßt, die aus organischen und/oder anorganischen bewuchsverhindernden Mitteln, Weichmachern, Hydrolyseregulern, Pigmenten, Lösungsmitteln und anderen herkömmlichen Zusatzstoffen ausgewählt werden können.

Revendications

1. Procédé de préparation d'une formulation de résine contenant un métal, caractérisé en ce qu'un mélange de
 - (A) une résine basique contenant un groupe acide,
 - (B) un sel métallique d'un acide organique à bas point d'ébullition, de 100 à 240 ° C, dans lequel le métal est choisi parmi les éléments ayant une valence de 2 ou davantage, et une tendance à l'ionisation inférieure à celle des métaux alcalins, et
 - (C) une acide organique monobasique à haut point d'ébullition possédant un point d'ébullition qui est d'au moins 20 ° C supérieur au point d'ébullition dudit acide organique à bas point d'ébullition, est mis à réagir à température élevée tout en extrayant du système l'acide organique à bas point d'ébullition formé.
2. Procédé selon la revendication 1, caractérisé en ce que le métal est choisi parmi les éléments appartenant aux groupes 1b, 11a, 11b, 111a, 111b, 1Va, 1Vb, Va, V1a, V1b, V11a et V111 du tableau périodique des éléments.
3. Procédé selon la revendication 2, caractérisé en ce que le métal est choisi parmi le zinc, le cuivre et le tellure.
4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que l'acide organique monobasique à haut point d'ébullition possède une propriété de protection contre la putréfaction.
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la réaction est effectuée en présence d'eau, tout en extrayant azéotropiquement avec cette eau l'acide organique à bas point d'ébullition formé.
6. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'acide organique à bas point d'ébullition est extrait à pression réduite.
7. Procédé selon l'une quelconque des revendication 1 à 4, caractérisé en ce que la réaction est effectuée en présence d'un solvant organique, l'acide organique à bas point d'ébullition étant extrait azéotropiquement du système avec ledit solvant organique.
8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que la résine basique contenant le groupe acide possède une concentration en équivalent acide de 25 à 350 mg KOH/g.
9. Utilisation d'une formulation de résine contenant un métal préparée par le procédé selon l'une quelconque des revendications 1 à 8 comme support résine d'une peinture anti-putréfaction, ladite peinture contenant éventuellement d'autres composant qui peuvent être choisis parmi les agent organiques et/ou inorganiques de protection contre la putréfaction, les plastifiants, les régulateurs d'hydrolyse, les pigments, les solvants et autres additifs classiques.